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Peculiarities of the Twinning in Silicon during Ball Milling in the Presence of Two Different Materials

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Abstract: The structure of silicon, along with mixtures of silicon and boron carbide (B_4C) powders and silicon and diamond powders with different proportions after mechanoactivation, has been studied by transmission electron microscopy (TEM) methods. It was shown that silicon and boron carbide experience twinning according to the known twinning mechanisms. In addition to the initial phase with a diamond lattice, the particles of two other phases were detected for silicon, including: the Kasper phase (SiIII) and lonsdaleite (SiIV). We established that the phase transformations in silicon can happen due to different mechanisms.

Keywords: silicon; mechanoactivation; Kasper phase; TEM; lonsdaleite

1. Introduction

The treatment of the powders of various materials by ball milling (BM) is widely used to produce nano-structured materials. Thus, the first step in producing nanostructured ceramics involves the high-intensity treatment of the initial materials to a size of 20 nm. The BM treatment is similar to the shock-wave treatment method. Both of these methods are used to obtain high-hardness carbides, borides and nitrides, with the aim of changing their structural state. It is known that during the processing of the powders of different materials, a range of defects can be observed, including cracks, dislocations, vacancies, stacking faults, etc. [1]. It is also known that milling leads to the formation of metastable phases [2]. Twinning was occasionally observed during the milling of powders [3]. In the present work, silicon was chosen as the object of investigation. Nanostructured silicon is a promising material due to its unique properties. Furthermore, nanostructured silicon is useful in various applications in thermoelectrics, membranes, etc. [4,5]. The presence of defects in the crystal lattice of a semiconductor affects the features of its band structure. In addition, the mechanical properties of the material strongly depend on the presence of defects [6]. The structure and properties of silicon depend on the mechanoactivation conditions and deformation medium. The modification of silicon by the nano-inclusions of the second phase (SiC, C_{60} and B_4C) leads to a slight change in the Seebeck coefficient but there is a 3-fold increase in the conductivity of the material [7]. In the present study, we treated both pure silicon and mixtures of silicon with boron carbide and diamond powder.

2. Experimental

Precursor components were treated in a Fritsch Planetary Micro Mill PULVERISETTE 7 premium line with a ceramic drum and Si_3N_4 milling balls until the size of the particles approached 10–15 nm. The obtained samples were studied using a JEM-2010 transmission electron microscope (TEM) with energy dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) attachments.

3. Results

At atmospheric pressure, silicon has a cubic diamond structure (SiI) with the lattice parameter a = 0.543 nm. At elevated pressures, 11 other crystalline phases of Si have been identified in the pressure cell experiments [8]. Two of the phases are referred to as the SiIII [9,10] or Kasper phase (a cubic structure with a = 0.663 nm) and the SiIV or lonsdaleite (hexagonal with a = 0.386 nm, c = 0.631 nm) phase [11]. These phases are metastable, persisting after the pressure release (unloading).

At the first stage, the silicon powder after treatment was analyzed by the TEM method. The duration of milling treatment was 5 min, 20 min and 2 h. After milling for 5 and 20 min, only powder grinding and cracking were observed. Twins were only formed after the 2-h treatment. Our studies have shown that a longer processing time does not cause any significant changes in either the structure or the properties of the material. Figure 1a shows cracks, which occurred in the silicon after treatment for 20 min. Figure 1b illustrates the two twinning systems in silicon after treatment for 2 h. The boundaries have a 70.53° angle. The twinning planes are traditional for silicon: {111}. Similar twinning after milling was also found in a previous study [3]. Furthermore, twinning is a structuring operation. Thus, the boundary layer of the twin atoms and two adjacent layers have an ABA sequence, which is an interlayer of another SiIV phase. In Figure 1, the rectangles indicate the fragments of lonsdaleite (SiIV) in a diamond lattice (SiI).

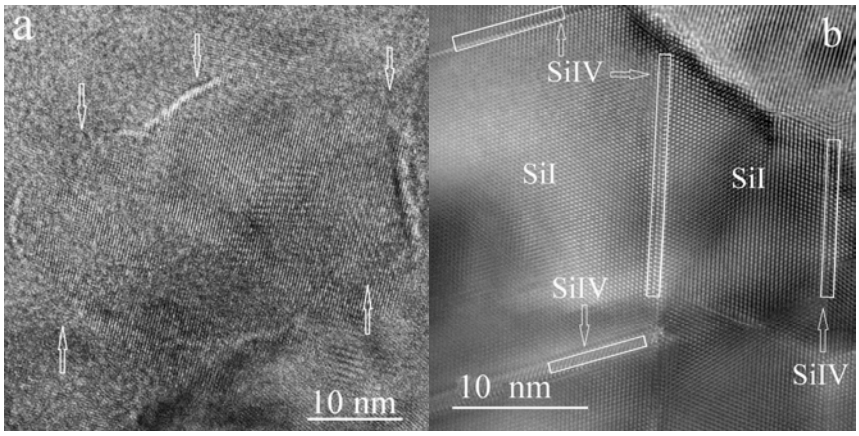

Figure 1. Defects in silicon:(**a**) cracks in Si after milling for 20 min; and (**b**) twinning in silicon after milling for 2 h. White rectangles mark the SiIV fragments.

A mixture of silicon and boron carbide is considered as a non-conventional nanomaterial because such material is promising for the development of thermoelectrics [12]. Therefore, in the next stage, we treated a mixture of silicon and boron carbide powders. In the beginning, we treated pure B_4C. We found cracks in the 10–15 nm particles after treatment. For boron carbide, no twinning, polytypes or other defects were detected after ball milling. Cracks were the only defect observed. At the same time, in the cases where there was a higher silicon concentration (about 95 wt% and higher), we observed both stacking faults and twinning in boron carbide. In other words, the deformation by twinning in boron carbide occurs in the environment of hundreds of silicon particles

The twins along the $\{10–11\}_h$ plane (in hexagonal coordinates) are similar to the deformation and growth twins observed in other previous works [13]. This is illustrated in Figure 2. Such behavior can

be explained by the role which silicon plays as a medium that transfers pressure and deformation to the boron carbide particles.

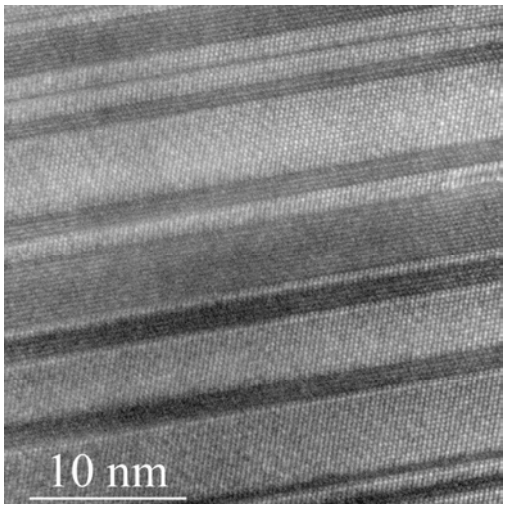

Figure 2. Twinning in B_4C.

The mechanisms of boron carbide deformation differ in the presence of silicon. When there is no silicon, the particles of boron carbide collide with each other. Since the hardness of silicon is lower than the hardness of B_4C [14], silicon acts as a soft damping material that separates the B_4C particles.

For comparison, in the next step, we treated silicon in the presence of diamond particles in the same proportions as before although we instead used a mixture of silicon and boron carbide. A diamond powder with a particle size of 30–50 nm was used. At a 50:50 ratio, some deformation bands, cracks, small-angle boundaries and Kasper phase fragments were noted in silicon. No twins were observed. This is due to the fact that a large amount of diamond powder leads to the destruction, refinement and amorphization of silicon. More interesting results were shown by the treatment of a 95 wt% Si: 5 wt% diamond. As a result, the TEM studies of the sample obtained after a two-hour treatment revealed twins in the silicon that are similar to those shown in Figure 1. Since the diamond concentration is low, the conditions resemble the grinding of pure silicon. Figure 3 shows the stacking faults in silicon.

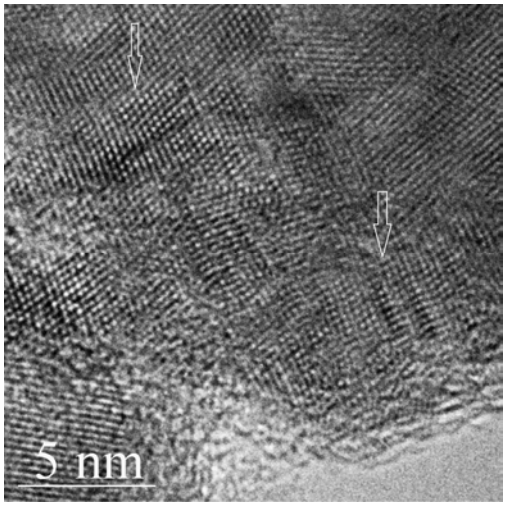

Figure 3. Stacking faults in Si after ball milling (shown by arrows).

In addition to twins and stacking faults, another interesting structure was obtained after this treatment (Figure 4). In the diamond lattice (SiI), fragments were observed with substantially increased distances between the (002) planes. The diffraction pattern contains an additional reflex, which corresponds to the increased distance between the (002) planes in SiI that is equal to 0.383 nm. These planes are shown by the arrows in Figure 4a. Apparently, in the process of deformation, a partial rupture of bonds occurred and a fragment of a new phase was formed. This distance corresponds to the (111) planes of the SiIII phase. As seen in the figure, the following orientation relationship (OR) is fulfilled: $(200)_{SiI}$ II $(111)_{SiIII}$. Such an OR does not correspond to any of the six variants considered in a previous study [15], which were obtained as a result of the assumption that the SiI → SiIV → SiIII transition occurs. In this case, a direct SiI → SiIII transition took place. Such direct SiI → SiIII transition was observed under the shear deformation at a pressure of 2–6 GPa and a temperature of 27 °C in a previous study [16]. A new OR occurs. However, apart from this fragment, the Kasper phase was also discovered in its pure form. Figure 5 shows a particle having a Kasper phase structure (SiIII).

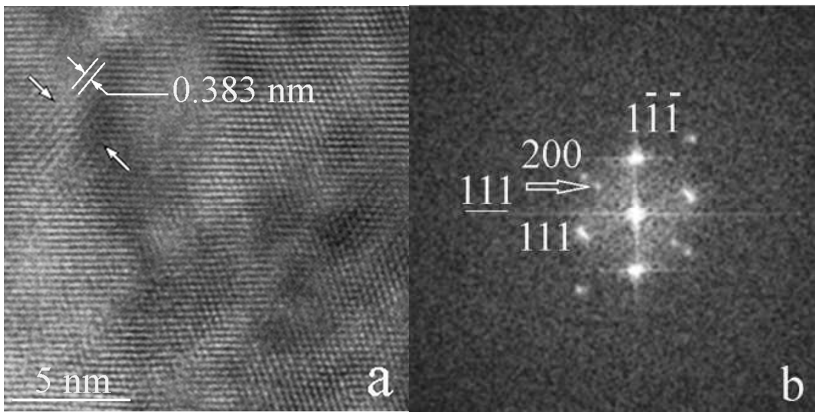

Figure 4. The structure of silicon treated in a mill with 5% of diamond powder: (**a**) Arrows show the planes with an increased interplanar distance of 0.383 nm; (**b**) These planes correspond to an additional reflex $(111)_{SiIII}$ in the diffraction pattern (denoted by an arrow).

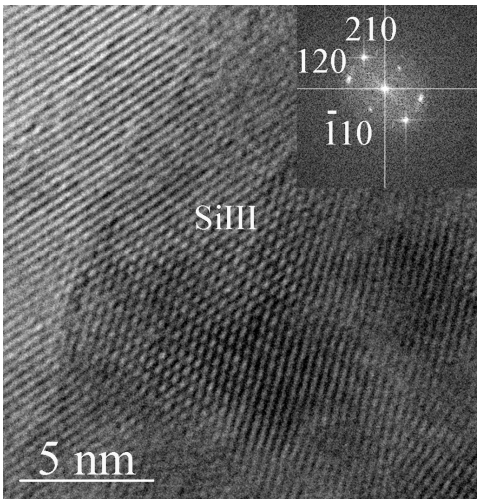

Figure 5. Kasper phase (SiIII).

4. Discussion

The features of twinning in a planetary mill involve multiple impact on the same particle. It is usually assumed that a variety of crystal defects, such as dislocations, vacancies, stacking faults and

so on, appears as a result of the deformation caused by mechanoactivation [1]. However, it is also known that ball milling is also capable of inducing structural transformations in solids.

It is difficult to compare the conditions for the formation of high-pressure phases obtained under thermobaric treatment using the appropriate conditions for the high-pressure phases obtained by milling. Nevertheless, the presence of the Kasper phase and lonsdaleite fragments in silicon indicates that considerably impressive values of temperature and pressure were achieved at the points where they formed, even if we take into account that the corresponding parameters for nanoparticles may differ significantly from the parameters for the large particles.

According to various estimates, the temperature of the milling balls can reach 500–600°C. These are average temperatures. After the impulsive compression of powder particles between the colliding milling tools, the local temperature can increase by an additional 50–300°C [17]. Under such conditions, even metastable phases can be formed, which usually exist at high pressures and/or temperatures. It was reported in a previous study [18] that pressures exceeding 8 GPa and temperatures exceeding 698 K can be achieved during BM. These estimates were made on the basis of the Hertzian impact theory [19].

It is believed that collision is the major factor generating over 94% of the energy transferred. The impact duration is approximately 10^{-5}s and the pressure at impact is 10^9 N/m^2. In a single collision, about 1000 grains of powder take part.

The deformation of silicon under the conditions of ball milling in many respects resembles the processes occurring under contact loading, indentation with hard indenters, scratching or machining [20]. The difference is that various particles undergo different processing and therefore, one can see a large number of defects and phases, such as the Kasper phase (SiIII) at different stages of its formation (Figures 3 and 4). It is interesting to note that the Kasper phase can be formed both by the SiI $\rightarrow$ SiIV $\rightarrow$ SiIII process [3,15] and the direct process (Figure 4). Previously, twins in silicon have been reported, such as the growth twins formed by the molecular beam epitaxial growth in a previous study [21]. Twins can be clearly visible after the nanoscratching [22] and nanoindentation [11] of silicon. Twins can also appear after shock load, under shear deformation and/or high pressure and after high-pressure release.

Twins can also appear after shock load, under shear deformation and/or high pressure and after high-pressure release. At the same time, despite the peculiarities of the ball milling treatment observed for the samples of silicon and boron carbide, it was confirmed that the twinning planes remain conventional for these materials.

5. Conclusions

It has been shown that the planetary mill treatment of silicon both in its pure form and in the presence of boron and diamond carbide additives results in the appearance of twins in silicon and in boron carbide, while the twins are formed along the same twinning planes in a conventional deformation. In the diamond powder, twinning was not detected. The formation of the Kasper phase (SiIII) and lonsdaleite (SiIV) was established. It was shown that during such treatment, different variants of phase transformations occur in silicon.

Author Contributions: M.Y.P. and D.A.O. processed the samples using the planetary mill treatment. B.A.K., I.A.P. and V.D.B. carried out TEM studies. All the authors have taken part in discussions and in the interpretation of the results and have read and approved the final manuscript.

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Conflicts of Interest: The authors declare no conflicts of interest.

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